Development, Processing, and Testing of High-Performance Corrosion-Resistant HVOF Coatings

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Abstract - *New amorphous-metal and ceramic coatings applied by the high-velocity oxy-fuel (HVOF) process may reduce the waste package materials cost of the Yucca Mountain high-level nuclear waste repository by over $4 billion (cost reduction of 27 to 42 %). Two critical requirements that have been determined from design analysis are protection in brines that may evolve from the evaporative concentration of pore waters and protection for waste package welds, thereby preventing exposure to environments that might cause stress corrosion cracking (SCC). Our efforts are directed towards producing and evaluating these high-performance coatings for the development of lower cost waste packages, and will leverage a cost-effective collaboration with DARPA for applications involving marine corrosion.*

I. INTRODUCTION

Man-made materials with up to 10,000 Year Service are needed for the construction of items such as the waste package, support pallet, drip shield, ground support, and invert (Figure 1). Alloy 22 & 316NG are now believed to have sufficient performance for the construction of safe and long-lived waste packages, but are extremely expensive. Some other applications of cost saving measures utilizing HVOF coatings are also shown in Figure 1. It is estimated that the 70,000 MTHM to be emplaced in the repository will require approximately 11,000-15,000 waste packages costing $4-6 billion, 11,000-15,000 support pallets costing $600-800 million, and 10,000-13,000 titanium drip shields costing $3-4 billion. The total estimated is therefore estimated to be approximately $8-11 billion dollars. Additionally, the degradation and failure of the ground support and invert could also have costly consequences. The rapid wear of cutting teeth on the Tunnel-Boring Machine (TBM, one to two machines will likely be used continuously during the life of the repository – about 30 years) require frequent maintenance and interruption in tunneling operations, thereby substantially increasing costs. If new, relatively inexpensive, high-performance materials and processes can be found and proven suitable, the life cycle costs for the proposed high-level waste repository at Yucca Mountain could be dramatically reduced. A novel strategy is proposed here that would use advanced high-velocity oxy-fuel (HVOF) structural amorphous metal (SAM) coatings to reduce the $58-billion life-cycle cost of the repository. Amorphous metal coatings lack grain boundaries and consequently are expected to have reduced corrosion rates. In particular lack of grain boundaries limits nucleation of pitting-type corrosion, which can be particularly detrimental to corrosion resistance.

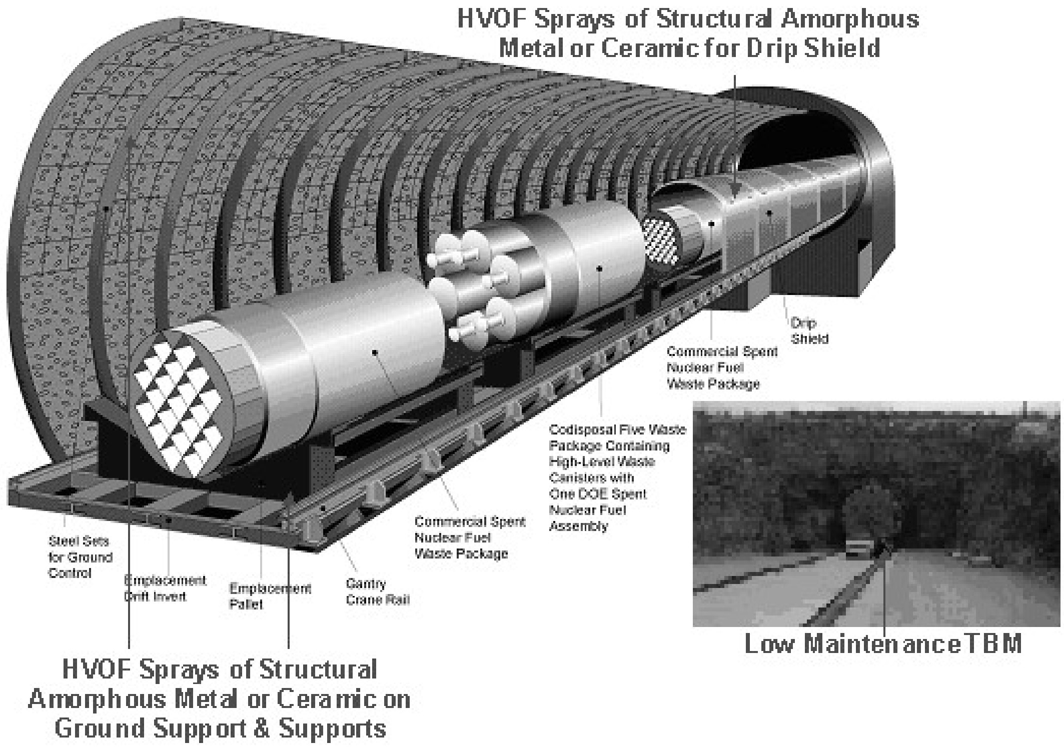


Figure 1. Applications of low-cost high-performance materials in the emplacement drifts.

II. HVOF AMORPHOUS-METAL COATINGS

Computational materials science will be used to design a new class of high-performance corrosion-resistant structural amorphous metal (SAM) coatings. These coatings will be deposited with the high-velocity oxy-fuel (HVOF) process, and enhanced through the application of high-density infrared fusing (HDIF). This strategy is illustrated with Figure 2.

These materials are expected to have densities close to that of wrought materials. While the amorphous metal alloys that have already been produced have exhibited incredible mechanical properties, including order-of-magnitude enhancements of mechanical strength, hardness and wear resistance, unusual self-sharpening characteristics, and good corrosion resistance, substantial improvement in corrosion resistance is still needed.

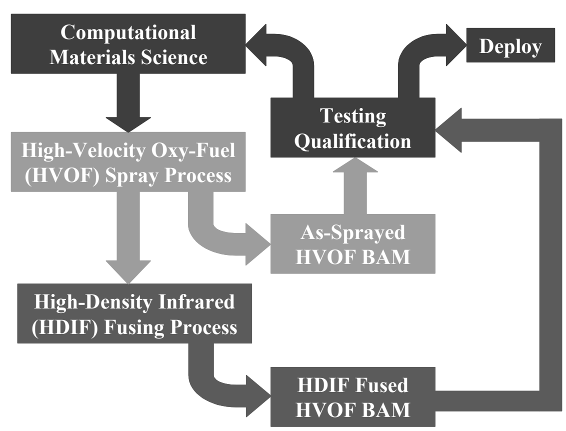


Figure 2. Strategy for the production of high-performance corrosion-resistant structural amorphous metal (SAM) coatings, using computational materials science for formulation design, HVOF for deposition, and HDIF for performance enhancement.

Exceptional corrosion resistance will also have to be demonstrated before these materials will achieve their full potential in repository applications. This work is directed at the further development and optimization of HVOF SAM coatings that will possess the corrosion resistance of high performance materials such as 316L stainless steel, alloys 600, 625, C-4, C-276 and C-22, and various grades of titanium. Several classes of amorphous metal formulations exist. For example, classical metal-metal systems include copper-zirconium and copper-titanium formulations. Transition metal-metalloid systems include Fe, Co or Ni as the transition metal, and P, Si, C or B as the metalloid. Significant enhancement of the corrosion resistance has been achieved through the elimination of the grain boundaries, with additional performance achieved through optimization of the composition. For example, the addition of Cr, Mo or Ti to Fe-13P-7C has enabled passive film formation during anodic polarization in 0.1 H_2SO_4. These alloys showed no pitting during testing in 3% NaCl solution.

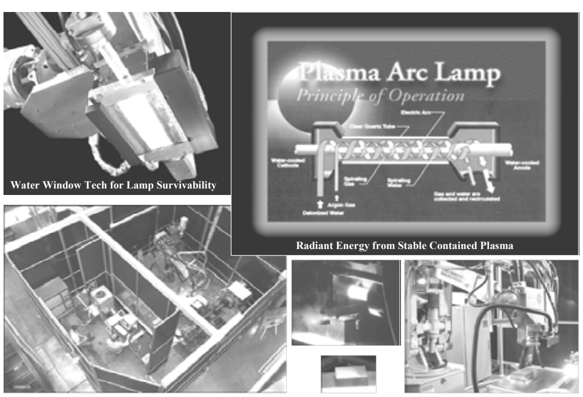


Figure 3. High-density infrared fusing (HDIF) will be used to eliminate porosity in HVOF SAM coatings, which will thereby enhance the durability and corrosion-resistance of these high-performance thermal-spray coatings.

III. MATERIALS DEGRADATION STUDIES

Two amorphous metal alloys that have been developed previously include iron-based chromium alloys, DAR 35 and DAR 40. Unlike 316L stainless steel, these alloys have virtually no nickel. The presence of substantial concentrations of molybdenum and tungsten are believed to stabilize the passive film formed under acidic and oxidizing conditions. In preliminary investigations, the corrosion resistance of 316L, DAR 35, and DAR 40 has been measured (Figure 4). The DAR 35 and 40 HVOF SAM coatings are more resistant to localized corrosion in seawater than 316L stainless steel. However, a higher corrosion current than 316L is observed in the DAR 35 and DAR 40 HVOF SAM coatings. This has been attributed to the rough as-sprayed surface of the amorphous metal coatings, which can be seen in Figure 5. The larger surface area of the coating surface along with the positive radius of curvature of portions of the “splat” cooled amorphous metal particles increases the corrosion current relative to a flat surface. Further optimization of the HVOF spray conditions could yield a smoother, more uniform surface with less surface area.

Under proper spraying conditions it is expected that these HVOF coatings are impervious to liquids; however, it has been demonstrated that high intensity infrared energy can be used to fuse the surface of the coatings to yield an even lower porosity in the coating. This has been named High-density infrared fusing (HDIF). Photographs of typical HDIF equipment are shown in Figure 3. This equipment has been developed at Oak Ridge National Laboratory. It is anticipated that the infrared fusing process can reduce the surface area of the coating and reduce the measured corrosion currents during electrochemical polarization measurements. It seems likely that in a long-term corrosion environment that the corrosion resistant alloy coatings would eventually smooth out under corrosion action and that the surface would become much smoother with a smaller surface area as long as no pitting or localized corrosion occurred. If this is the case, the larger corrosion current measured for the as-sprayed coatings would be an initial transient corrosion effect that would diminish after some amount of time in the corrosion environment.

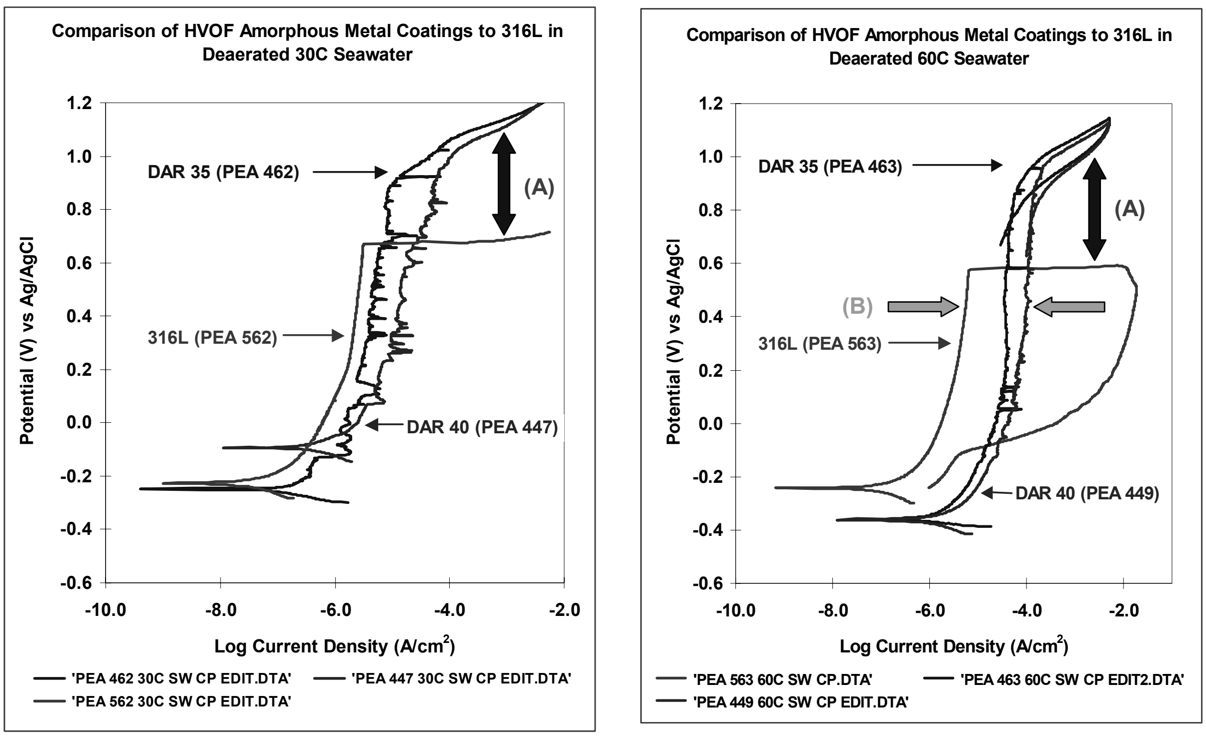
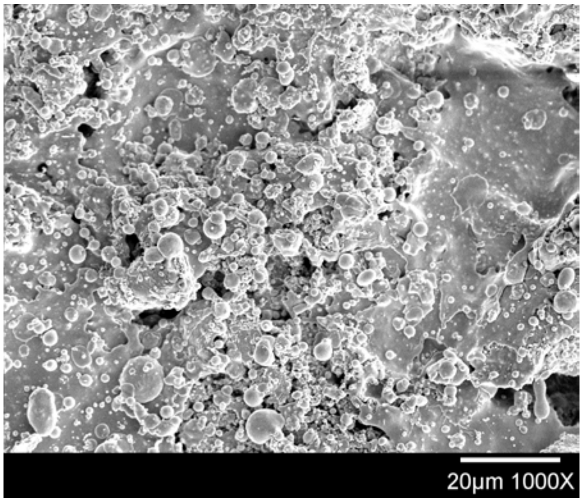


Figure 4. Cyclic polarization has been used to determine the localized corrosion resistances of 316L stainless steel (PEA 562) and HVOF SAM coatings (PEA 462 and 447) in seawater. The arrows, marked A, show that the transpassive potentials for the HVOF SAM coatings are much higher than that of 316L stainless steel. In fact, the threshold potential for breakdown of the passive films on these HVOF SAM coatings may lie above the thermodynamic limit of water. The higher apparent passive current density of the coatings is attributed to the greater surface roughness of these thermal spray coatings, and should not be interpreted in terms of a rate of corrosion. These measurements in seawater are shown to provide comparison with other materials measured in seawater. Other results in different aqueous environments have been obtained but are not reported here.



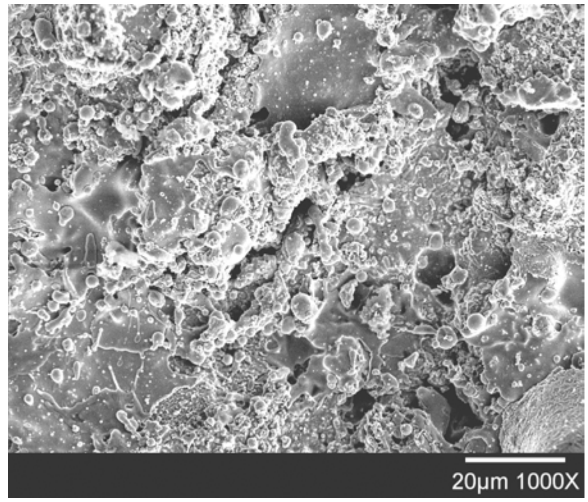


Figure 5. Electron micrographs of DAR35 and DAR40, respectively, showing the as sprayed coating. Large amounts of extra surface area are present on the surface due to incompletely flattened particles on the surface. Potentially, spraying parameters could be optimized further. Long-term corrosion of these coatings would eventually flatten the coating, which should reduce corrosion rates.

IV. FUTURE WORK – LEVERAGING HVOF PROCESS EXPERIENCE TO PRODUCE CERAMIC COATINGS

A second related approach, the application of ceramic coatings with HVOF, could produce even greater cost savings. Such ceramic coatings are fully oxidized materials, and offer corrosion resistance that is not possible with classical metallic alloys. Some groups have now postulated extremely threatening waste package surface environments, such as boiling saturated calcium chloride solutions. These extreme environments are said to evolve during the evaporative concentration of synthetic pore water. Furthermore, thermal decomposition of these brines could produce volatile acid gas. The best known metallic alloys may not provide adequate performance if these extreme and unlikely conditions are accepted as plausible environments by regulatory agencies. Novel approaches, such as the use of HVOF ceramic coatings may be the only viable engineering material capable of withstanding such aggressive conditions.

A variety of ceramic coatings have been developed to prevent the corrosion of carbon steel substrates. These protective coatings can be applied by conventional plasma spraying, or by a high-velocity oxy-fuel (HVOF) process. As shown in Figure 6, ceramic coatings produced with the high-velocity oxy-fuel (HVOF) process have little interconnected porosity, whereas coatings produced with conventional plasma spray can have substantial interconnected porosity, and make poor barriers to corrosion. After exposure of carbon steel samples with HVOF coatings to brine at 90°C for six months, no corrosion was observed at the metal-ceramic interface. This is in sharp contrast to the corrosion observed with the conventional plasma sprayed coatings shown in Figure 6.

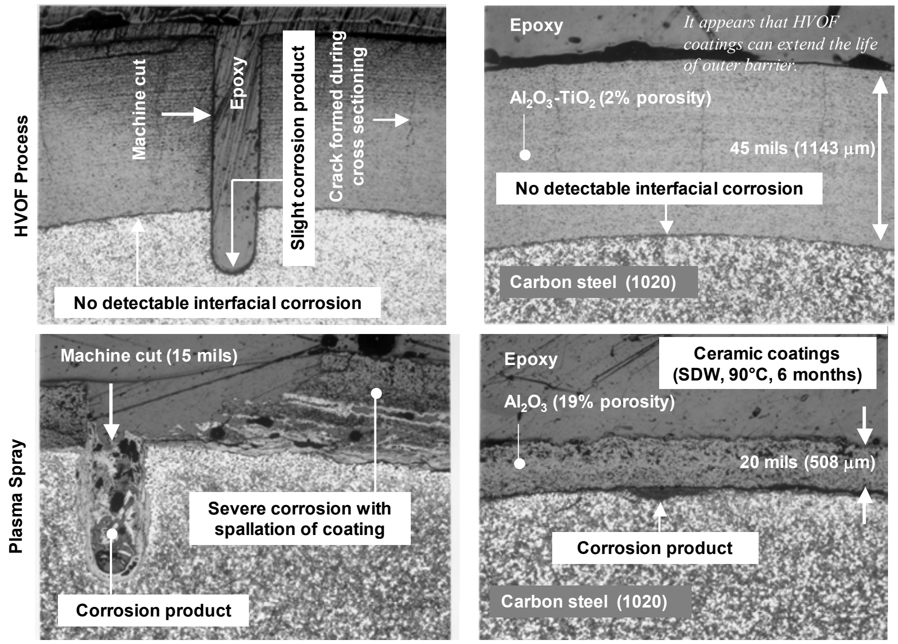


Figure 6. Ceramic coatings produced with the high-velocity oxy-fuel (HVOF) process have little interconnected porosity, whereas coatings shown here that were produced with conventional plasma spray have substantial interconnected porosity, and make poor barriers to corrosion. After exposure of carbon steel samples with HVOF coatings to brine at 90°C for six months, no corrosion was observed at the metal-ceramic interface. This is in sharp contrast to the corrosion observed with the conventional plasma sprayed coatings.

V. SUMMARY

Amorphous metal alloys are being developed for corrosion resistant coatings to potentially reduce costs of engineering materials in the proposed Nuclear Waste Repository. These coatings may provide corrosion resistance for long-term resistance to varying corroding environments. High Velocity Oxy-Fuel thermal spraying is being used to apply an impervious, nominally dense coating of these amorphous metals. This is possible due to the high quench rate of metal particles applied by the HVOF process. Initial corrosion measurements on HVOF coatings applied to substrates indicates that transpassive corrosion potentials exceeding that obtained from stainless steel 316L are possible with the two amorphous metal alloys examined thus far. It is anticipated that further improvements in corrosion resistance will be obtained by utilizing a High Density Infrared Fusing process to reduce porosity and surface roughness in the as-sprayed amorphous metal coatings. On-going work with HVOF sprayed ceramic coatings has also shown excellent resistance to the corrosion of plain carbon steel samples.

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